

EFFECT OF SOLVENT INDUCED SWELLING ON THE RESISTIVITY OF POLYBUTADIENE-CARBON BLACK-GRAPHITE COMPOSITES

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1. Introduction

A new analysis that describes the change on electric properties of polymeric composites, filled with conductive aggregates, during organic solvent absorption processes is introduced in the present work. Figure 1 shows a simplified typical electric circuit arrangement. In this configuration, the solvent diffusion process into the composite gradually changes its electric conductivity, following the solvent concentration profile along the sample radius over a period of time. In order to model the previous situation, the following hypotheses were considered:

- I) Solvent diffusion process on the sample is one-dimensional, taking place only along the radial direction (axial diffusion is neglected).
- II) The polymer matrix and the organic solvents are dielectric materials.
- III) Solvents are absorbed only by the polymer matrix, and not by the conductive aggregates.
- IV) Solvent diffusion into the composite follows Fick's Law (this is especially true on elastomer matrix composites and copolymers).

Using those hypotheses it is possible to predict, at constant voltage, the variation of the electric current on the composite during the solvent diffusion process. First of all, Ohm's Law can be written as:

$$I(t) = \int_0^{a(t)} \frac{E}{\rho_m(r, t) \cdot l} dA(t) \quad (1)$$

where $I(t)$ and $\rho_m(t)$ are the instantaneous electric current on the sample and local composite resistivity. $A(t)$, $a(t)$ and l are the transversal section, external radius and length of the sample. Finally E is the applied voltage, which remains constant.

Eq. 1 can be normalized as:

$$\frac{I(t)}{I_0} = \frac{2}{r_0^2} \int_0^{a(t)} \frac{\rho_{m0}}{\rho_m(r, t)} r(t) dr \quad (2)$$

where r is the radial coordinate and variables indexed with zero represent the state of the composite before the solvent gets in touch with it. In order to calculate the electric resistivity, it is necessary to know its relationship with the solvent volumetric fraction. This can be done by modifying a model proposed by McLachlan [11], which describes

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the conductive composite electric resistance change as a function of its conductive and dielectric volumetric fractions. This equation, which is known as the generalized effective media (GEM) model, integrates two morphology parameters: f_C (the critical percolative value of the conductive fraction) and q (an experimental exponent). Previous equation can be written as:

$$\frac{(1-f)(\rho_H^{-1/q} - \rho_m^{-1/q})}{\rho_H^{-1/q} + f_R \rho_m^{-1/q}} + \frac{f(\rho_L^{-1/q} - \rho_m^{-1/q})}{\rho_L^{-1/q} + f_R \rho_m^{-1/q}} = 0 \quad (3)$$

where ρ_H , ρ_L and ρ_m are the resistivities of the high and low resistive components and the composite resistivity respectively, f is the conductive fraction and f_R is given by the following expression:

$$f_R = \frac{1-f_C}{f_C} \quad (4)$$

It is important to mention that the GEM equation was deduced for a composite of only two components. However, we can use it if considering the following approximation; since the polymer matrix and organic solvents are both dielectrics with a resistivity of the same order of magnitude and substantially different from that of the conductive fraction, we may treat both phases (polymer and solvent) as an unique phase. Therefore, the sum of the polymeric matrix fraction, f_P , plus the solvent fraction, f_S , will be named as the non conductive fraction. This last approximation is possible because the resistivity is one of the physical magnitudes that present the broader range of values. Indeed, the resistivity of common organic substances varies typically between 10^{16} to 10^8 ohms-cm, while the conductive aggregates have conductivities between 10^{-1} to 10^{-7} ohms-cm.

To evaluate $f(r,t)$ on each location as function of time, the following relation was considered:

$$\begin{aligned} f(r,t) &= 1 - f_P(r,t) - f_S(r,t) = 1 - f_P(r,0) \frac{V_T(r,0)}{V_T(r,t)} - f_S(r,t) \\ f(r,t) &= 1 - f_P(r,0) \cdot [1 - f_S(r,t)] - f_S(r,t) \end{aligned} \quad (5)$$

where $V_T(r,t)$ is the local volume as a function of time.

The solution of Fick equation, considering previous conditions (7), is:

$$f_S(r,t) = \left(1 - \frac{2}{a(t)} \sum_{n=1}^{\infty} \frac{\exp(-D\alpha_n^2 t) J_0[r\alpha_n]}{\alpha_n J_1[a(t)\alpha_n]} + \dots \right) f_{S \max} \quad (6)$$

where $f_{S \max}$ is the insaturation solvent fraction, J_0 and J_1 are the first class Bessel functions, of zero and first order respectively, and α_n are the positive roots of $J_0[a(t)\alpha_n]$. The previous solution converges very well for medium and large times; however for short times it is needed a significant number of additional terms. An alternative is to use the following approximation for short times [16]:

$$f_s(r,t) = (\sqrt{a(t)}/r \operatorname{erfc} \frac{a(t)-r}{2\sqrt{Dt}} + [a(t)-r] \frac{\sqrt{Dt}}{4r\sqrt{ra(t)}} \operatorname{ierfc} \frac{a(t)-r}{2\sqrt{Dt}} + \dots) f_{s \max} \quad (7)$$

Using the previous equations it is possible to calculate $f(r,t)$, using the value of $f_s(r,t)$ in Eq. 5. Finally, to evaluate the increment of the filament external radius the following relation was deduced:

$$a^2(t) = a^2(0) + 2 \int_0^{a(t)} f_s(r,t) r dr \quad (8)$$

It is evident that it is not possible to get an explicit expression for $a(t)$ using the previous equations, however it is possible to evaluate this parameter employing a numerical method.

2. Results and discussion.

Figure 3 shows the percolation data of both composites. The continuous lines in this plot represent the best data fitted. Subsequently concentration profiles were evaluated for six different solvents, as a function of the radial coordinate at, different times. Figure 3, shows the relationship between the instantaneous radii and the initial one, for a series of different solvents. First of all, it is interesting to observe that on the studied case the moving boundary exhibits a very large variation, as the radii increases more than a 40%. As previously mentioned, for large swelling levels the diffusion coefficient may become concentration dependent, however the results obtained with a constant coefficient correlate satisfactorily with the experimentally observed data [14-15].

Figure 4 illustrates how the electric current curve falls with the solvent contact time, for each different solvent. It can be noticed that, in general, the current diminishes rapidly with time, at the exception of the first solvent, which is in good agreement with experimental observations [4, 7, 10, 14, 15]. As expected, the current intensity drops faster for solvents that have larger diffusion coefficients on the composite than for those that have smaller ones. Moreover, it is evident that the swelling curves of Figure 6 could fit in a master curve, if one changes the contact time (t) as the abscise variable by a dimensionless one as $Dt/a(t)^2$. Finally, it is important to mention that this methodology may allow a more precise sensor design, based only on easy obtainable laboratory data.

5. Conclusion

A methodology that describes the change on electric properties of polymeric composites, during solvent diffusion processes, is presented in this work. The equations that result from this methodology requires simple numerical procedures to be solved, and no numerical instability was observed during the process. The obtained results correlate very close the available experimental data, and therefore could be very useful for chemical sensor design.

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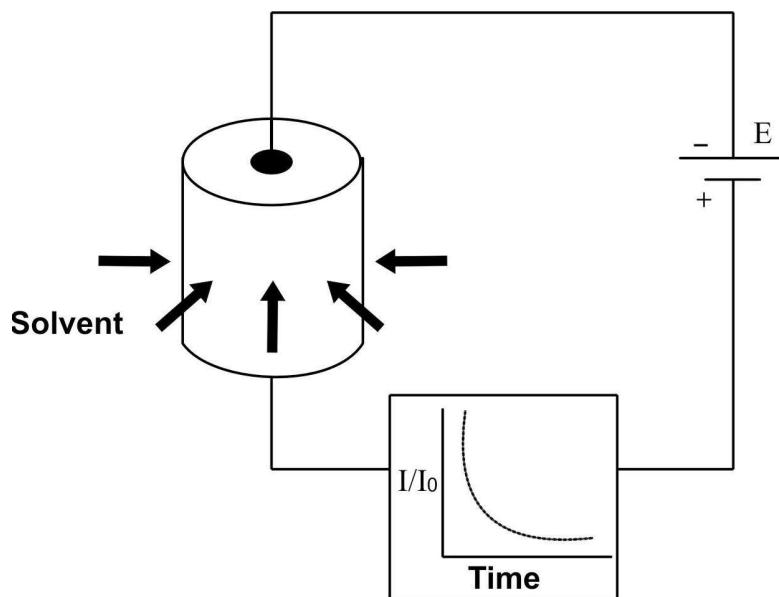


Figure 2.- Schematic of circuit for sensor testing

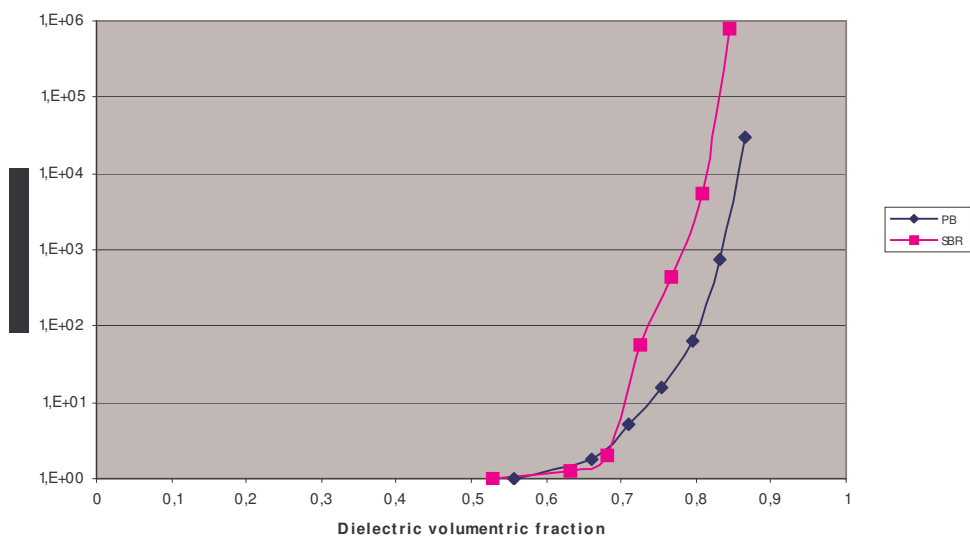


Figure 3.- Percolation curve for PB and SBR composites.

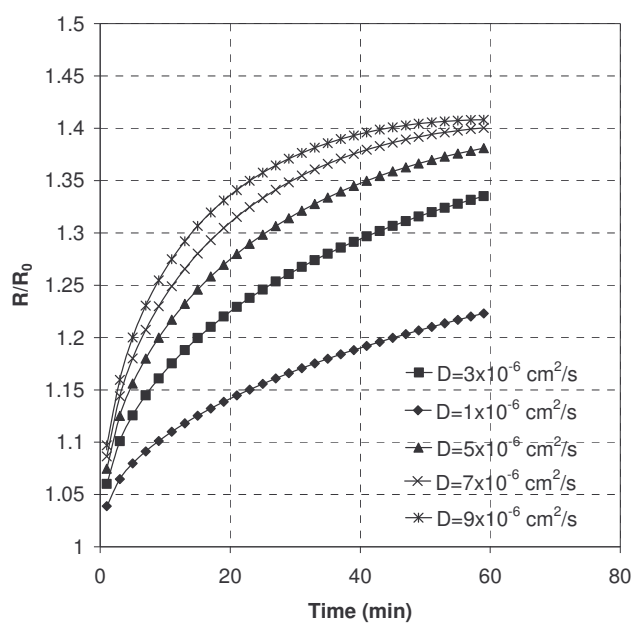


Figure 3.- Evolution of the instantaneous radii for different solvents

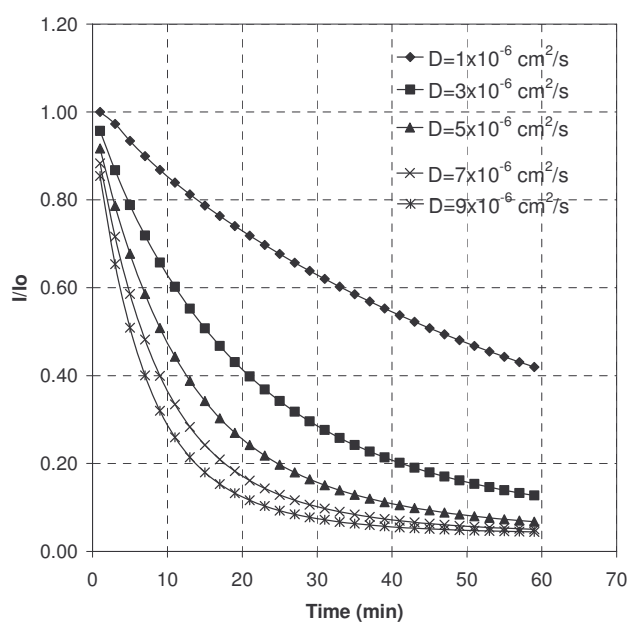


Figure 4.- Falling of the current intensity with the solvent contact time.